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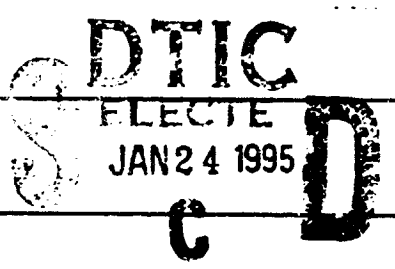
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE See Title Page	3. REPORT TYPE AND DATES COVERED 1 February 1987 to 31 January 1991

4. TITLE AND SUBTITLE Use Title on Reprint One Copy of Each Submitted	5. FUNDING NUMBERS N00014-87-C-0146 DRW 44C- 43031 4305 S4

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6. AUTHOR(S)   See Individual Articles

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Vanderbilt University Nashville TN 37332 (615-322-2786)	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660	10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES   Each Paper Summarized on first page. Journal articles submitted as contract reports. All work performed under Government contract

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release: distribution unlimited.	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)   See first page of Article

19960105 012

14. SUBJECT TERMS Free Electron Lasers Medicine Biology Biomedical Instrumentation, Energy Cells	15. NUMBER OF PAGES 00
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

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Gas-Exposure Enhanced Na* Emission from Na-Rich Surfaces

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Abstract: The optical emission attributed to electronically desorbed excited sodium atoms from NaCl and Na-evaporated surfaces is shown to be enhanced by exposure of the surface to gaseous CO_2 and N_2. This is the first observation of enhancement of electron-stimulated desorption of *substrate atoms* caused by the exposure of surfaces to gaseous molecules which do not contain the desorbed atoms. The large amount of excited sodium yield at 60 K provides evidence for non-existence of the secondary-electron excitation of thermally desorbed ground sodium.

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This work reports the first measurement of the influence of surface impurities on the electron-stimulated desorption of *substrate atoms*. The surface composition can be altered by the migration to the surface of either substrate atoms or bulk defects.[1-3] Atomic or molecular adsorbates on surfaces may originate by exposure of the surfaces to gaseous molecules whose atomic constituents are either the same as, or chemically derived from, the dosed molecules.[4-6] It is quite understandable that external gas exposure enhances desorption yield of adsorbates since the dosed molecules increase the adsorbate concentration. Recently, the experiments of Johnson and co-workers[7] and the calculations of Nordlander[8] show that the probability of hydrogen-atom desorption from metal surfaces can be altered by the presence of impurities on the surfaces. An immediate expectation is that the probability of *substrate-atom* desorption may also be enhanced by the presence of surface impurities. In this paper we show that excited sodium atom emission is dramatically increased when the electron-bombarded sodium surface is exposed to gaseous CO_2 and N_2 molecules. This observation indicates that gas exposure plays an important role in electronic erosion of substrates and is significant to such applications as lithography, surface catalysis, and the analysis of surface damage.

The work was carried out in an UHV system, which operates at a base pressure of 1.0×10^{-10} Torr. Gases were admitted to the chamber through two Varian leak valves allowing the partial pressures of two gases, CO_2 and N_2, to be controlled in the range of 1.0×10^{-10} to 1.0×10^{-6} Torr. Electron gun was operated in the energy range 10 to 400 eV at typical currents of 10-150 μA. The samples were mounted on a micromanipulator allowing them to be moved relative to the optical detection system. The samples were in thermal contact with both a closed-cycle helium cooler and a heating unit; sample temperatures could be varied from 50 to 800 K. The alkali-halide crystals were cleaved in air, mounted with their (100) surfaces facing the beam and heated under UHV conditions

for cleaning. Thick sodium metal layers were obtained by evaporation from SAES sodium dosers onto a glass slide. Electron bombardment of a surface produces optical emission partially attributed to electronic transitions of desorbed excited species from the surface. Optical emission from the samples was imaged onto the entrance slit of a McPhereson 0.3-m monochromater. Photons were detected by a cooled photomultiplier, operated in a pulse-counting mode. The stepping motor for control of the grating and the scaler for photon counting were interfaced through CAMAC and IEEE-488 units to an Apple Macintosh computer.

The results of the experiment are presented in Figures 1-2. Figure 1(a) and (a') compare optical spectra arising from an electron-bombarded NaCl surface without and with gas dosing. Initially without external gas exposure, a freshly cleaved NaCl sample was cooled to 60 K and pre-irradiated by 300-eV electrons for about 12 hours. Figure 1(a) displays a large amount of bulk fluorescence arising from this surface under electron bombardment. There was no observable Na^* emission. Later, after the surface was exposed to 30 langmuirs of a 1:1 gaseous mixture of CO_2 and N_2, a large Na^* desorption yield appeared, as shown in Figure 1(a'). Figure 1(b) and (b') shows the similar observation for sodium metal surfaces. The difference between the sodium-metal and the NaCl experiments is that, to obtain the above results, electron pre-irradiation was required for the NaCl surfaces but not needed for the sodium-metal surfaces. The data for the both substrates clearly show that gas exposure can influence electron-stimulated desorption of substrate atoms even though the atoms are not chemically related to the dosing molecules. As seen in the figure, we also observe enhancement of the ESD yield of excited CN molecules. The CN enhancement is understood to be due to the increasing concentration of adsorbed CN when the surface is exposed to CO_2 and N_2.[9]

The detailed growth process of the excited sodium desorption yield has been examined for various gas-exposure times. The desorption yield of excited sodium atoms from a Na-metal surface under 110 μA, 300-eV electron bombardment increases as a function of the CO_2 and N_2 exposure time, as shown in Figure 2. The yield for excited sodium increases faster than linearly with the exposure. The yield for excited CN desorption, also shown in Figure 2, increases slower than linearly with the exposure and the growth tends to saturate at large exposures. Although the CO_2 and N_2 exposure enhances both CN* and Na* desorption yields, there is an important difference between the enhancements. For CN* desorption, the exposure is required to increase the concentration of the CN adsorbates on the surface. The saturation yield in the CN growth is understood to be due to a saturation of the surface sites for CN formation and an equilibrium between the formation of surface CN and the CN related desorption.[9] However for Na*, there is an abundance of sodium atoms on the surface since these are substrate atoms. The saturation limit observed in CN molecules does not appear for excited sodium desorption in the exposure range investigated here.

Many studies of electron and photon stimulated desorption (ESD and PSD) of excited alkali atoms from alkali-halide surfaces have been carried out.[10-13] There are long-standing arguments about whether the production of excited alkali atoms come from the secondary electron excitation of *thermally* desorbed ground-state alkali atoms. The some experimental results[10,11] support this mechanism as follows: 1) the velocity distribution of excited sodium atoms follows a Boltzmann distribution agreeing with the surface temperature, and 2) electronic state populations of excited sodium atoms agree with the populations observed in gas-phase electron-impact excitation cross sections for sodium. On the other hand, some experiments[12,13] show that excited-alkali production in PSD decreases as the temperature increases while ground-state production of alkali atoms

4

increases as the temperature. Although the secondary electron excitation mechanism may be important for some high temperature experiments, it cannot explain this difference. Our data show that the yield of excited sodium production at 60 K is very large, even larger than the yield at 300 K. At such a low temperature, it is impossible to produce thermal ground-state sodium desorption followed by secondary electron excitation in such a large amount. A direct desorption induced by excitation to some repulsive electronic state, and/or production due to chemical reactions on the surfaces may be responsible for the production of excited sodium metal.

It is extensively documented that electron[10, 14, 15] bombardment can induce accumulation of excess metal on alkali halide surfaces. Thus, we believe that the pre-irradiation for NaCl is required to produce metallization of the alkali halide surface. It is generally believed that a metal surface is difficult to produce the metal atom desorption since the initial excitation energy is quickly dissipated to the bulk. This is consistent with our data, which show no excited sodium desorption from sodium metal and Na-rich NaCl surface under electron bombardment.

CO_2 and N_2 exposure to the Na-rich surface produces impurities of the surface. These oxygen, carbon, and nitrogen impurities residing on the sodium surface may form sodium compounds, such as sodium oxide or insulator monolayers/multilayers on the metal surface. Nordlander theoretically predicted[8] and Johnson and co-workers observed[7] that probability of excited hydrogen atom desorption is enhanced by coadsorbed impurities on metal surfaces. We postulated that a similar picture may apply to the present result which shows enhancement of substrate atom desorption due to coadsorbed impurities on the sodium surfaces. Formation of the sodium-impurity complex localizes incident energy and consequently enhances the probability of the sodium desorption.

In summary, this is the first observation that electron-stimulated desorption of substrate atoms is enhanced by exposing the surface to gaseous molecules whose atomic constituents differ from the desorbed atoms. This observation indicates that nature of surface bonds plays an important role in electronic erosion. In addition, the large amount of excited sodium desorption at 60 K roles out the second electron excitation mechanism.

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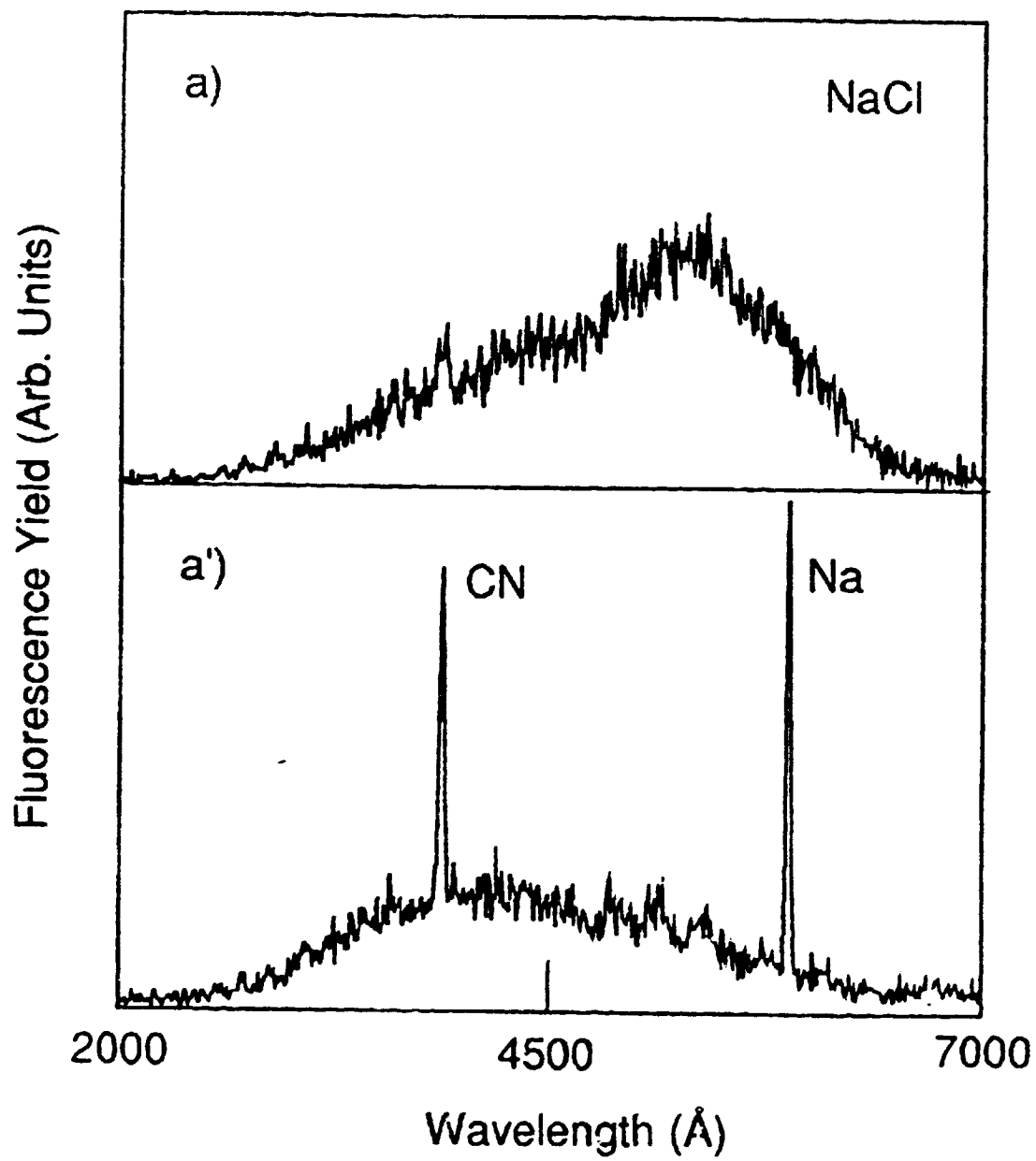
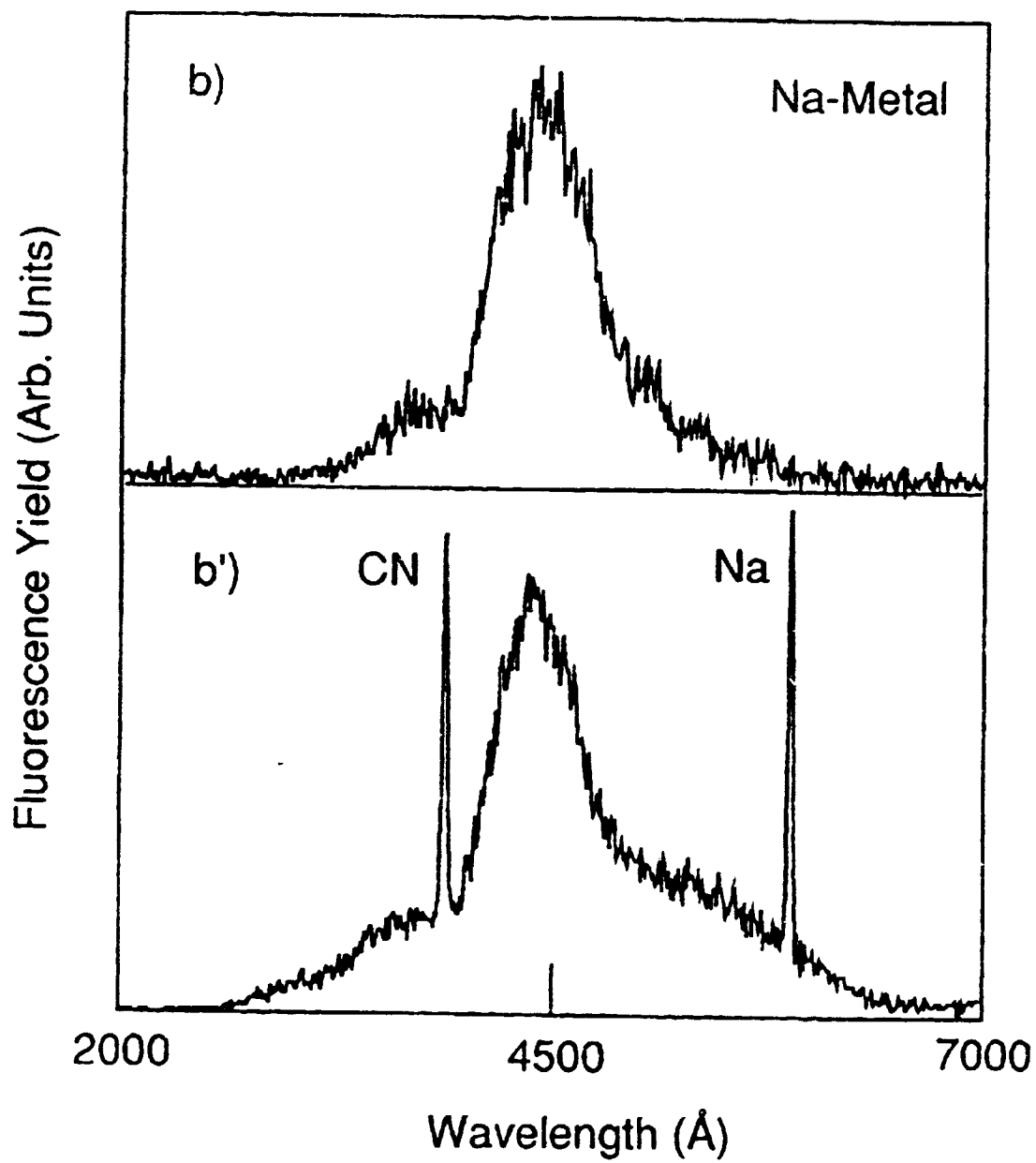[14]P. Wurz and C. H. Becher, Surf. Sci. **224** (1989) 559.

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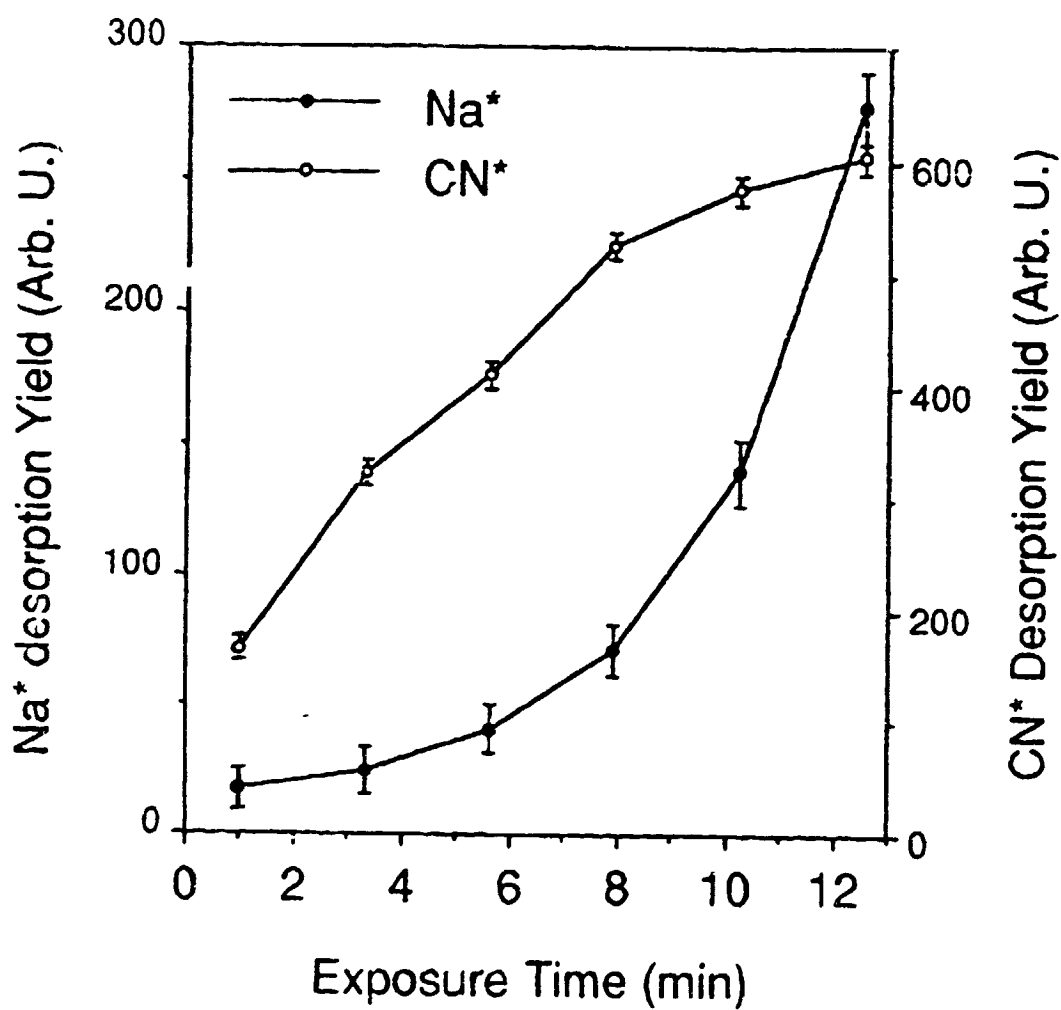
Figure Captions:

Figure 1. Optical emission spectra due to 300-eV electron bombardment (a) on a pre-irradiated NaCl surface at 60 K, (a') on the surface with $CO_2+N_2(1:1)$ exposure at 5.0 x 10^{-8} Torr, (b) on a sodium metal surface at 60 K, (b') on the surface with $CO_2+N_2(1:1)$ exposure at 5.0 x 10^{-8} Torr.

Figure 2. Excited sodium and CN desorption yields from a sodium-metal surface at 60 K plotted as a function of time exhibiting the influence of gas exposure, $CO_2+N_2(1:1)$ at 1.0×10^{-07} Torr.

a) NaCl

a') CN   Na

Fluorescence Yield (Arb. Units)

2000   4500   7000

Wavelength (Å)

b)   Na-Metal

b')   CN   Na

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